

# Kinetic and Mechanistic Studies of B-N Hydrogenation/Dehydrogenation

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University of Washington

May 2005

Project ID #  
STP9

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# Overview

## Timeline

Project start date: FY05

Project end date: FY09

*New Start*

## Budget

Total project funding (requested):

\$ 1.1 M DOE share

\$ 0.28 M Cost Share

Funding from FY05:

\$171 K (DOE + Cost Share)

## Barriers Addressed

Weight and Volume

Efficiency

Regeneration Processes

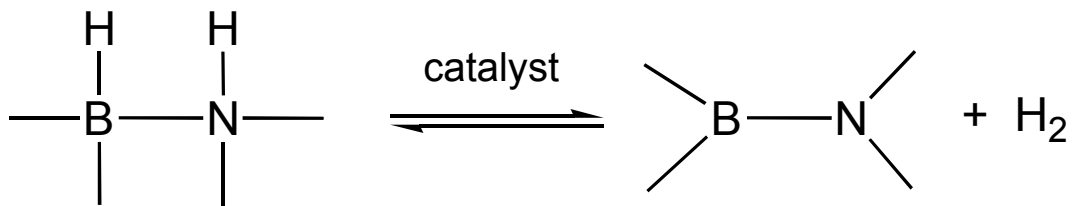
Amineboranes offer high hydrogen storage capacity in principle, but thermal hydrogen release from amineboranes is erratic and inefficient. Effective catalysts for dehydrogenation/ hydrogenation of BN are needed.

## Partners

DOE Center of Excellence for  
Chemical Hydrogen Storage

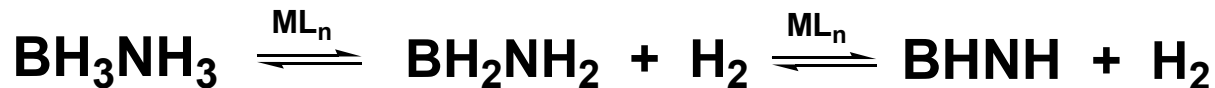
# Kinetic and Mechanistic Studies of B-N Hydrogenation/Dehydrogenation

**Objectives:** To understand the mechanism(s) of amineborane dehydrogenation and B-N hydrogenation and to use this insight to develop catalysts exhibiting satisfactory rates to allow for efficient hydrogen storage.



# Why are Mechanistic Studies Needed?

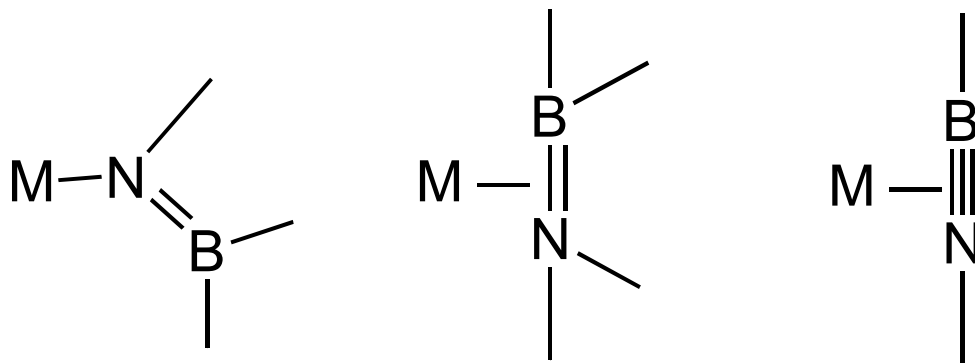
Metal complexes catalyze dehydrogenation/hydrogenation of BN materials.



**HOW?**

Detailed mechanistic studies using well-characterized models of likely intermediates will lead to improved catalysts. This work will be synergistic with the amineborane work being carried out by COE partners at LANL, PNNL and Penn.

# Task 1 - Prepare Metal Complexes with B-N Ligands



Select substituents to stabilize analogs of metal imine, alkene and alkyne complexes.

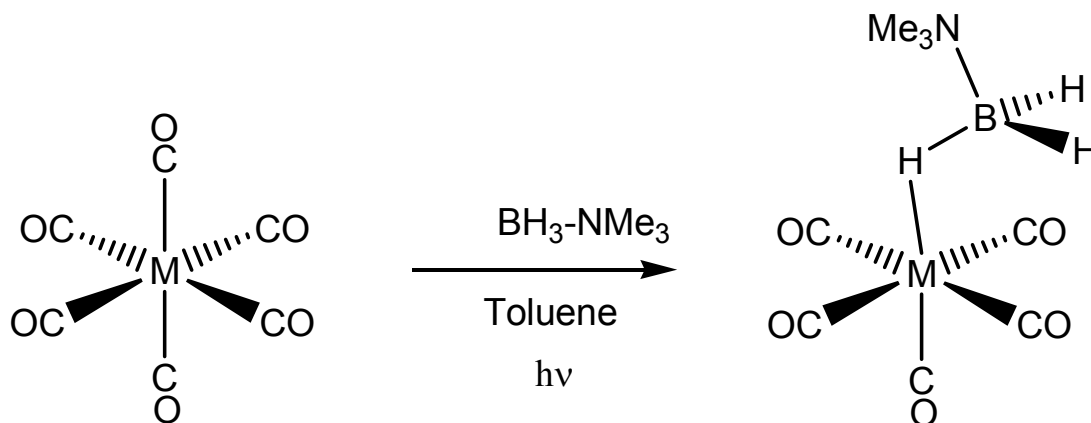
Characterize and investigate the reactivity of these novel species.

# Our Plan: Generate Ligand Deficient $L_nM$ Species to Observe Coordination of B-H Bonds

- Generation of unsaturated  $L_nM$  species by photolysis and chemical means in the presence of  $Me_2NHBH_3$ ,  $PhNH_2BH_3$  and  $NH_3BH_3$ .
- Reactions will be monitored by  $^1H$  and  $^{11}B$  NMR at low temperature.
- Low temperatures are needed to prevent dehydrogenation.
- Problems anticipated: poor solubility of  $NH_3BH_3$  in non-coordinating solvents, possible dehydrogenation of the amineborane which would lead to the formation of the corresponding dihydrogen or dihydride complex.

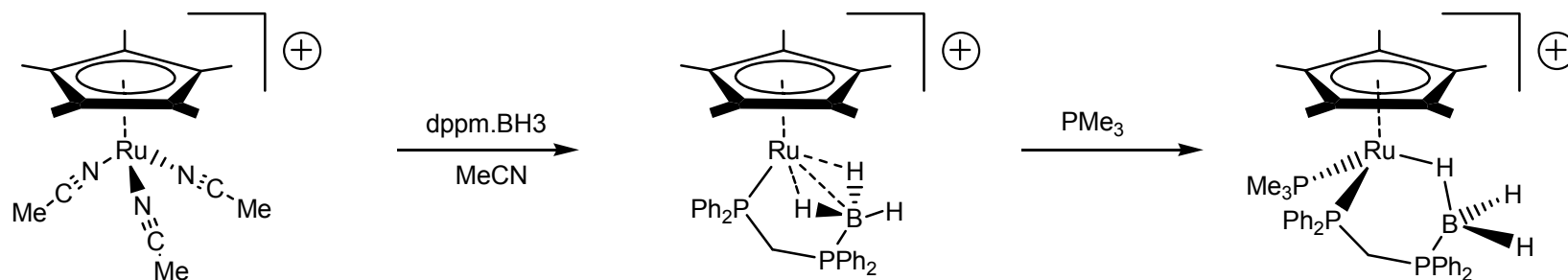
# Example of a Transition Metal Complex of an Amineborane

Shimoi *et al.* have isolated a series of borane adduct complexes of chromium and tungsten  $[(OC)_5M(H_3B-NMe_3)]$  ( $M = Cr, W$ ).



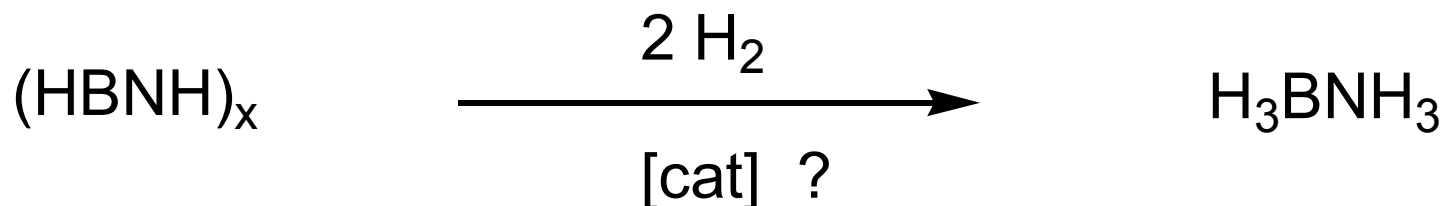
# Example of a Ruthenium Borane Complex

Weller and coworkers reported the synthesis of a complex with a chelating phosphine borane ligand.





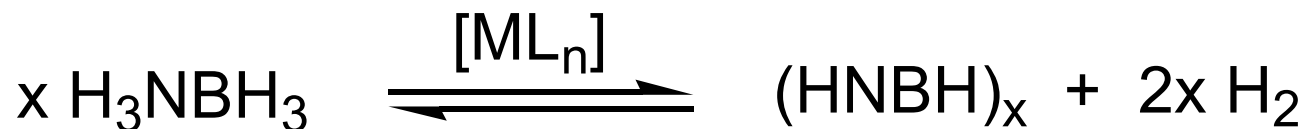
## Task 2 - Investigate Reactivity of Hydrogen Deficient B-N Species with H<sub>2</sub>



Reactivity studies with different metal complexes will help identify different mechanisms and best catalysts.

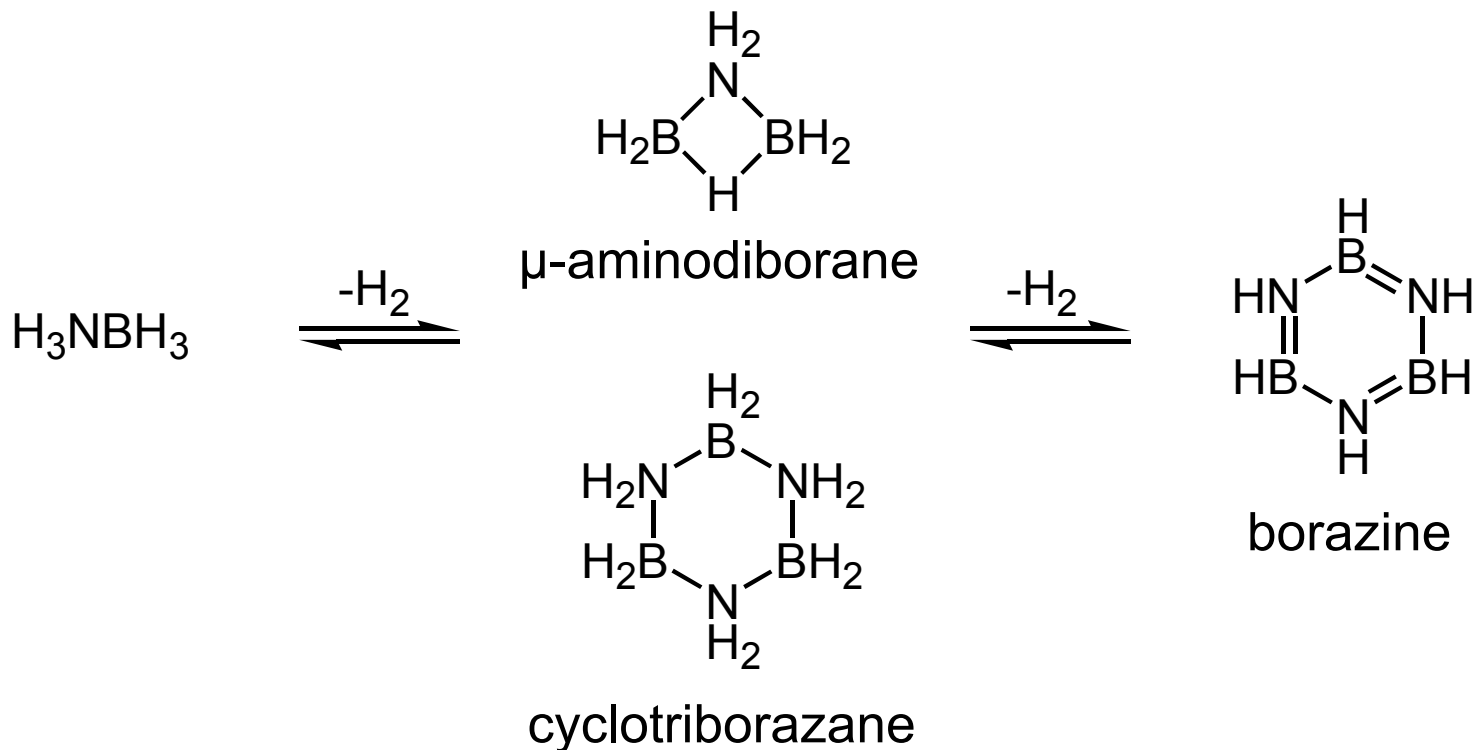
# Task 3 - Screen Homogeneous Catalysts for Hydrogenation/Dehydrogenation of B-N Model Compounds

Use Task 1 & 2 results to identify and test both platinum group metal and non-PGM catalysts.



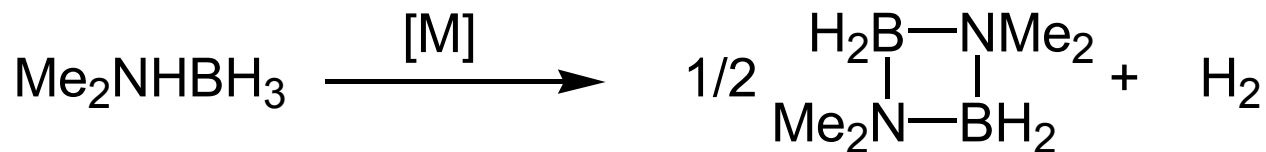
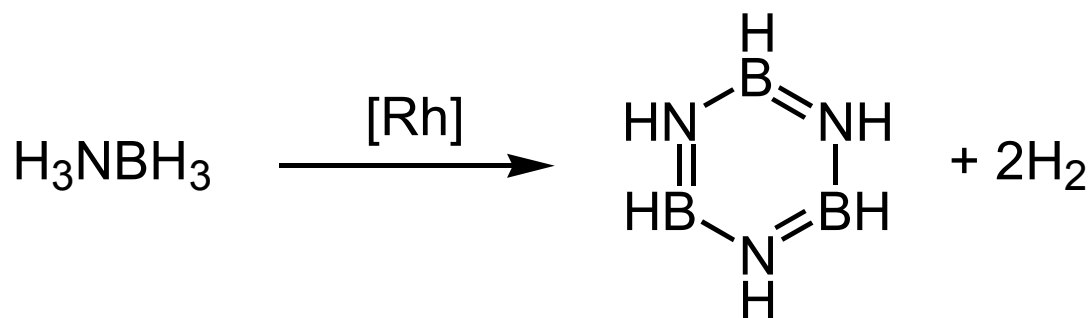
# Thermal Dehydrocoupling of $\text{H}_3\text{N}-\text{BH}_3$

Ammonia-borane undergoes thermal decomposition at high temperatures to borazine, accompanied by hydrogen evolution. Intermediates include cyclotriborazane and  $\mu$ -aminodiborane (oligomers of  $\text{H}_2\text{NBH}_2$ ).



# Catalytic Dehydrocoupling of Aminoboranes

Dehydrocoupling of  $\text{H}_3\text{NBH}_3$  and  $\text{Me}_2\text{NHBH}_3$  occur under mild conditions in the presence of various transition metal catalysts.



Jaska, C. A.; Manners, I. *J. Am. Chem. Soc.* **2004**, *126*, 9776 (and references therein).

Chen, Y.; Fulton, J.; Linehan, J.; Autrey, T. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* **2004**, *49*, 972.

Chen, Y.; Fulton, J.; Linehan, J.; Autrey, T. *J. Am. Chem. Soc.* **2005**, *127*, 3254.

## **Task 4 - Screen Non-PGM Catalysts for Activity with Amineborane Derivatives**

Coordinate with other Center partners to apply new non-PGM catalysts to complex boranes and other amineborane derivatives.

# Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

- The rapid buildup of high pressures of hydrogen in dehydrogenation reactions with successful catalysts.

# Hydrogen Safety

Our approach to deal with this hazard is:

- Reactions will be carried out on small scale.
- The maximum amount of hydrogen pressure will be calculated and the safety of the reaction assessed prior to commencing experiments.

# Timeline of Project Tasks

	Year 1	Year 2	Year 3	Year 4	Year 5
<b>Task 1:</b> Prepare and characterize metal complexes with B-N ligands.					
<b>Task 2:</b> Explore homogeneous hydrogenation of B=N model complexes and study mechanisms.					
<b>Task 3:</b> Screen and identify PGM and non-PGM catalysts for BN hydrogenation/ dehydrogenation reactions in model complexes.					
<b>Task 4:</b> Screen and identify PGM and non-PGM catalysts for BN hydrogenation/ dehydrogenation reactions of $\text{BH}_3\text{NH}_3$ and polymeric $(\text{BH}_2\text{NH}_2)_n$ .					

Select most promising catalyst